

Development Status of a Rapid-Cold-Start, On-Board, Microchannel Steam Reformer

**DOE Hydrogen, Fuel Cells & Infrastructure Technologies
Program 2004 Peer Review Meeting**

**Greg A. Whyatt
May 25, 2004**

**Team Members: Kriston Brooks, Jim Davis, Chris Fischer, Dave King,
Larry Pederson, Susie Stenkamp, Ward Tegrotenhuis**

This presentation does not contain any proprietary or confidential information.

Objectives

- ▶ Utilize microchannel steam reformer and vaporizer to demonstrate rapid cold start of the steam reforming sub-system.
- ▶ Develop a prototype microchannel-steam-reforming fuel processor at ~2 kWe scale that will meet DOE performance targets when scaled up to 50 kWe.

Performance Criteria	2004 Projected Performance	2004 Demo Target
Cold (20C) Start Time	12 sec, reformer only	<60 s to 90%
Start up Energy	<7 MJ (a)	2 MJ
Power Density	2300 W/L (a)	700 W/L
Efficiency	78%	78%

(a) based on individual components only, excludes tube, duct, insulation etc.

- ▶ Develop reactors, vaporizers, recuperative heat exchangers, and condensers broadly applicable to other fuel processing options.
- ▶ Engage industrial partner(s) to facilitate application of technology to full-scale fuel processing systems.

Budget

- ▶ Continuing Project, \$119K of Carryover Funding
- ▶ FY04 Funding Level \$700K, allocated:
 - \$400K funding for reforming activities (this presentation)
 - \$300K for WGS development (poster session)

Technical Barriers and Targets

- ▶ Fuel-Flexible Fuel Processor Technical Barriers Addressed
 - I. Fuel Processor Startup/Transient Operation
 - M. Fuel Processor System Integration and Efficiency

- ▶ Key DOE Technical Targets Addressed:
 - Cold (20°C) Startup Time
 - 2004 target <60 seconds to 90% traction power
 - Ultimate target <30 seconds to 90% traction power
 - Warm Transient Response
 - 2004 target <5 sec (10% to 90% or 90% to 10%)
 - Ultimate target <1 sec (10% to 90% or 90% to 10%)
 - Start-up Energy
 - 2004 target <2 MJ at 50 kWe
 - Ultimate target <2 MJ at 50 kWe

Approach to Developing Fast Start Ability

- ▶ Use micro-channel steam reformer and water vaporizer to minimize thermal mass.
- ▶ Configure reactor and vaporizer as thin panels to minimize combustion side pressure drop, allowing high combustion flow.
- ▶ Assemble reforming subsystem test unit and demonstrate rapid cold start.
- ▶ Transition to high temperature reforming to further reduce reformer mass, minimizing startup energy.

Project Safety

- ▶ Training of staff on laboratory-specific hazards is assured by limiting access via IOPS (Integrated Operations System)
- ▶ Test plans reviewed/approved by safety and facility staff.
- ▶ The microchannel architecture has low internal volume, which minimizes flammable gas inventory.
- ▶ Steam reforming is endothermic → no runaway reactions
- ▶ A single relay shutdown switch included in all experiments.
- ▶ Automated shutdown and alarm capability included for unattended operation.

Reforming Development Timeline



First Microchannel steam reformer

FY 1999

Fast SR kinetics observed in a microchannel reactor



10kWe Reforming System

FY 2000

Designed and built 10 kWe SR with integrated HX network



First low-dP vaporizer prototype

FY2001

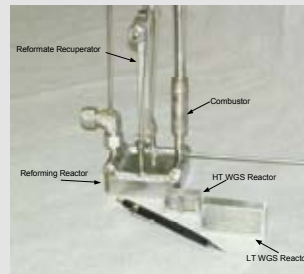
10 kWe reactor testing
First "low dP" vaporizers
Modular test stand established



Reforming Test Stand for capacities up to 2 kWe.

FY 2002

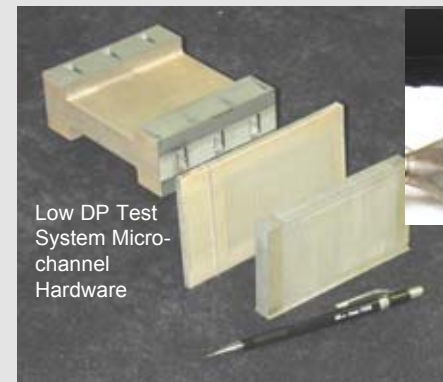
Modular Test Stand Testing
SR fuel flexibility, durability testing
Full-scale low dP vaporizers delivered



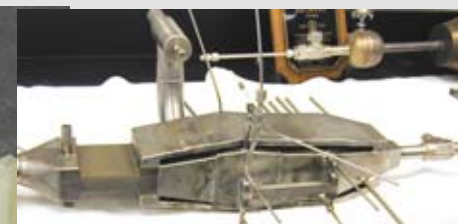
High Temperature Reformer with WGS reactors

FY 2003

Investigate high temperature reforming kinetics and sulfur tolerance. Fabrication of first low-dP reforming reactor.



Low DP Test System Micro-channel Hardware



Low DP Test System

FY 2004

Low-dP Gas-Gas Recuperator
Low-dP reforming and rapid cold start demonstration.
Recuperator/mixer provided for ANL 10 kWe ATR.



ANL FASTER Recuperator

Low-dP steam generator for 50 kWe ATR system.

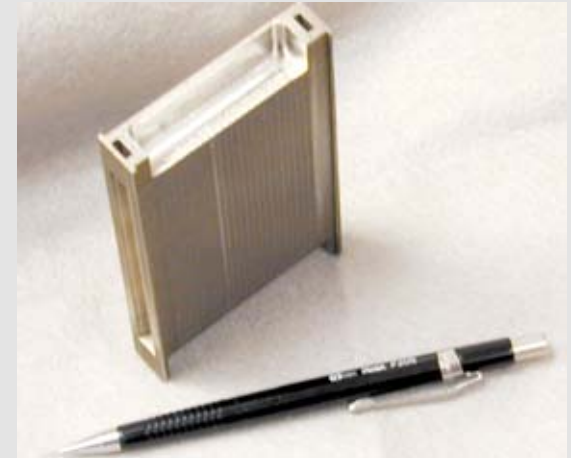


Changes Made to Achieve Fast Start

- ▶ Low dP configuration is used on reactor and vaporizer. Allows increased combustion gas flow.
- ▶ Fuel is directly injected into steam. This eliminates the mass and thermal transient associated with the fuel vaporizer.
- ▶ High temperature air recuperator eliminated. Previously located between the reformer and vaporizer, the recuperator was eliminated to prevent the thermal mass from affecting the start-up transient behavior.
- ▶ The low-temperature air recuperator has been enlarged to retain efficiency. The low-temperature recuperator does not need to reach operating temperature in order to achieve full reformat production.
- ▶ Combustion is now non-catalytic and spark ignited. Provides lower pressure drop and faster startup.

Advantages of Low-dP Reformer (compared to previous configuration)

- ▶ **Low pressure drop** ($\sim 1''$ H₂O) at steady state reduces parasitic power drain associated with air movement. During startup, high gas flow does not produce excessive pressure drop.
- ▶ **Elimination of metal header** eliminates lag between ignition and heat delivery to reaction channels on combustion side.
- ▶ **Initial heat delivery is uniform** across all reaction channels – reduces transient time to achieve quality reformat during cold start.
- ▶ **Higher inlet combustion temperatures** can be tolerated without excessive metal temperatures – efficiency and startup energy advantages.



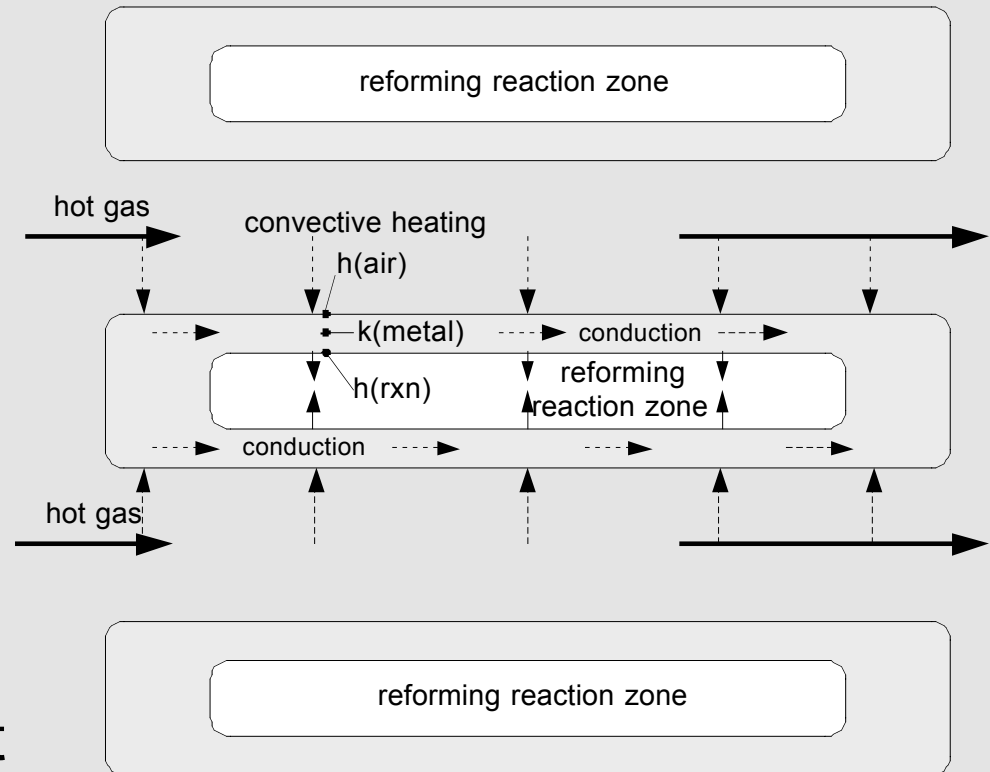
Low-dP Reformer



Previous Configuration

Low-dP Reformer – Tolerance of Higher Inlet Temperatures

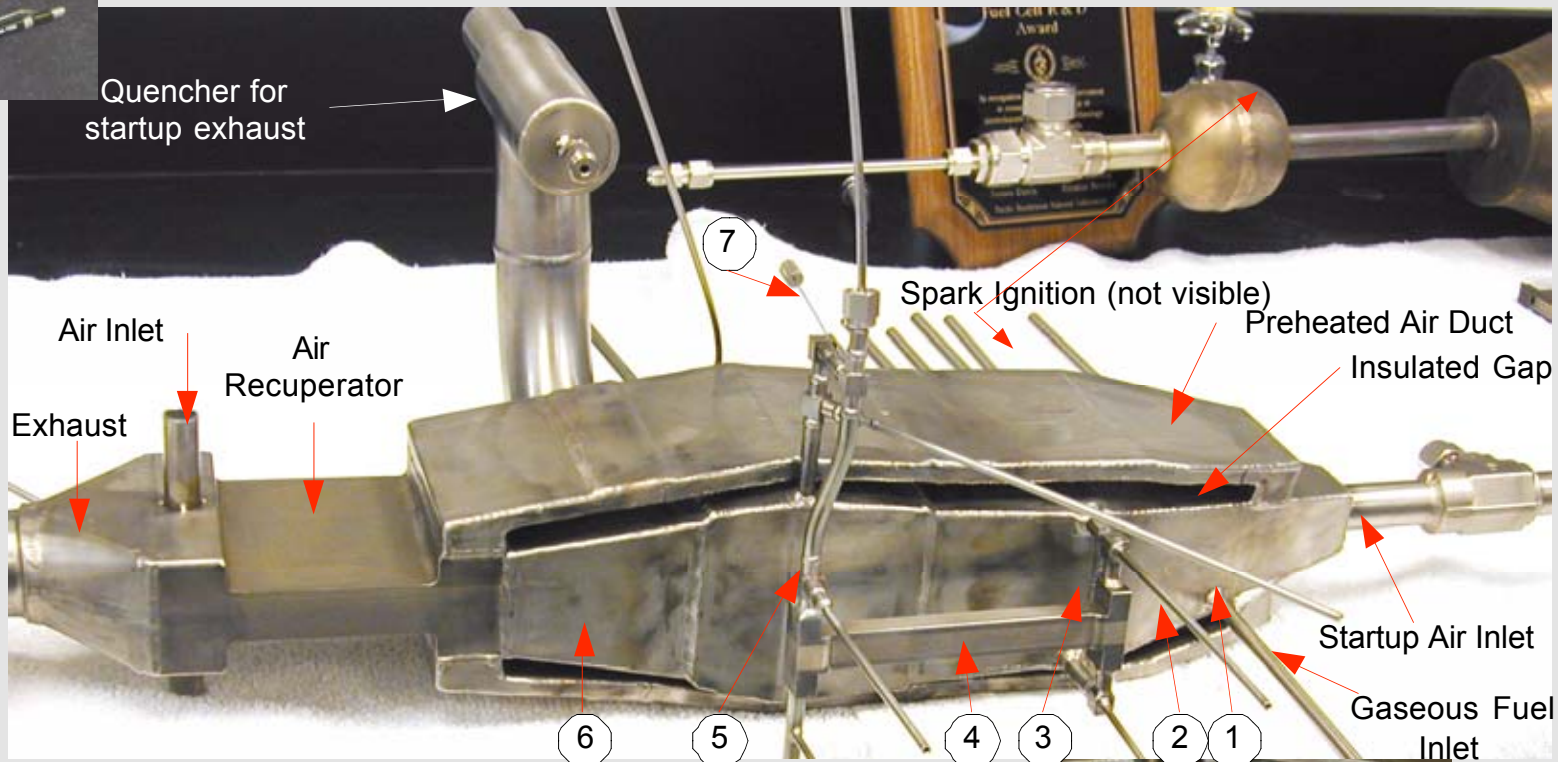
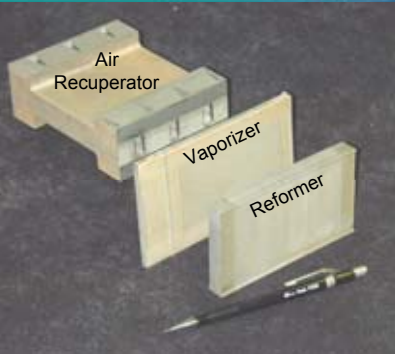
- ▶ By controlling $h(\text{rxn}) > h(\text{air})$ metal temperature can be held near reforming temperature, allowing higher gas inlet temperature.
- ▶ Thin panel allows conduction to reduce metal temperature gradient, allowing higher gas temperatures without excessively high metal temperatures.



Cross Section of Low-dP Reformer

(reforming flow is into the plane of the diagram)

Initial Fast-Start Test System

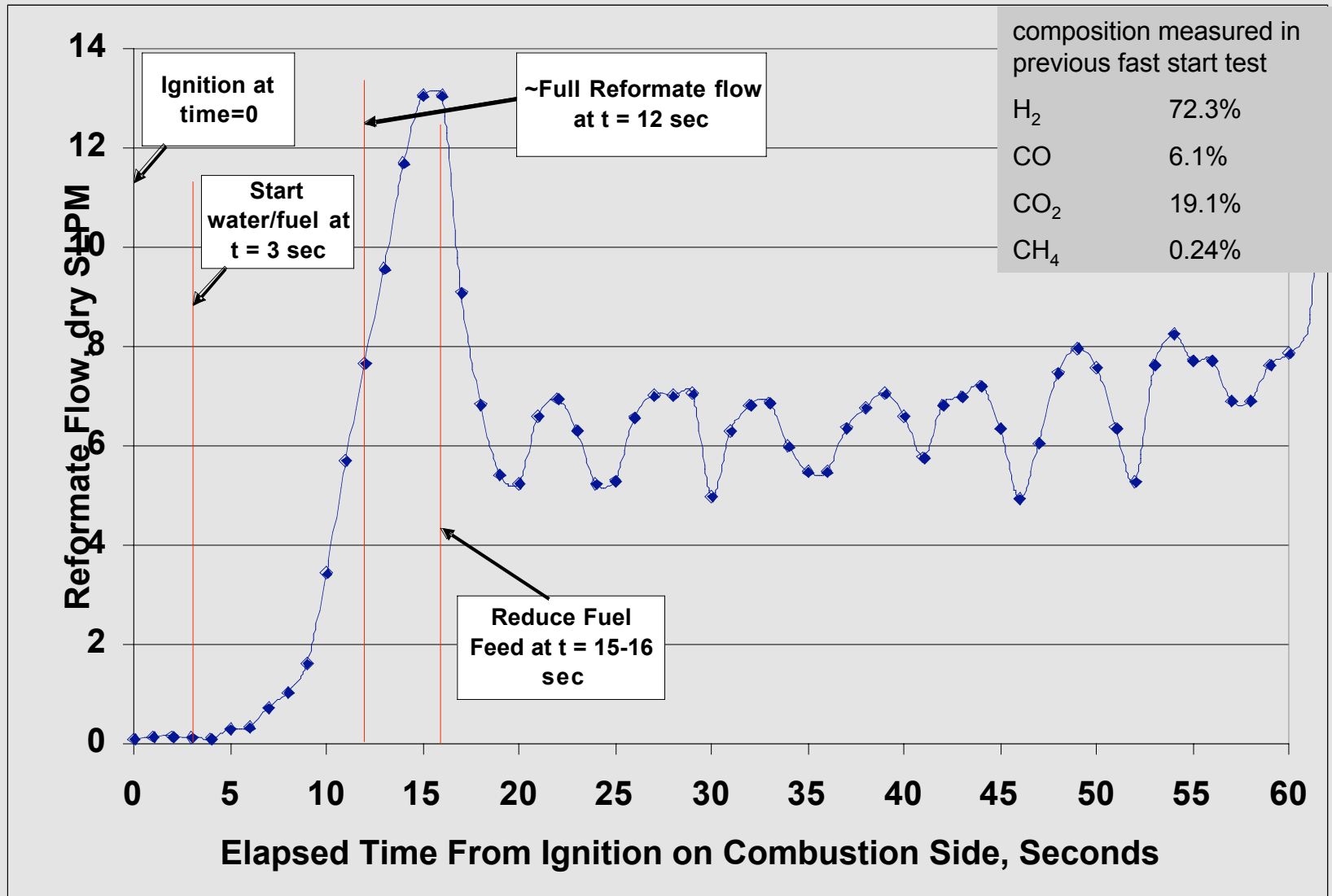


- 1 = location of mixer for mixing gaseous fuel into startup air stream
- 2 = location of combustion chamber (inside duct)
- 3 = location of panel reactor (inside duct)
- 4 = microchannel recuperator, heated by steam during startup
- 5 = location of water vaporizer (inside duct)
- 6 = exhaust duct carrying gases exiting the water vaporizer
- 7 = injection point for fuel to be reformed (atomizes liquid into steam)

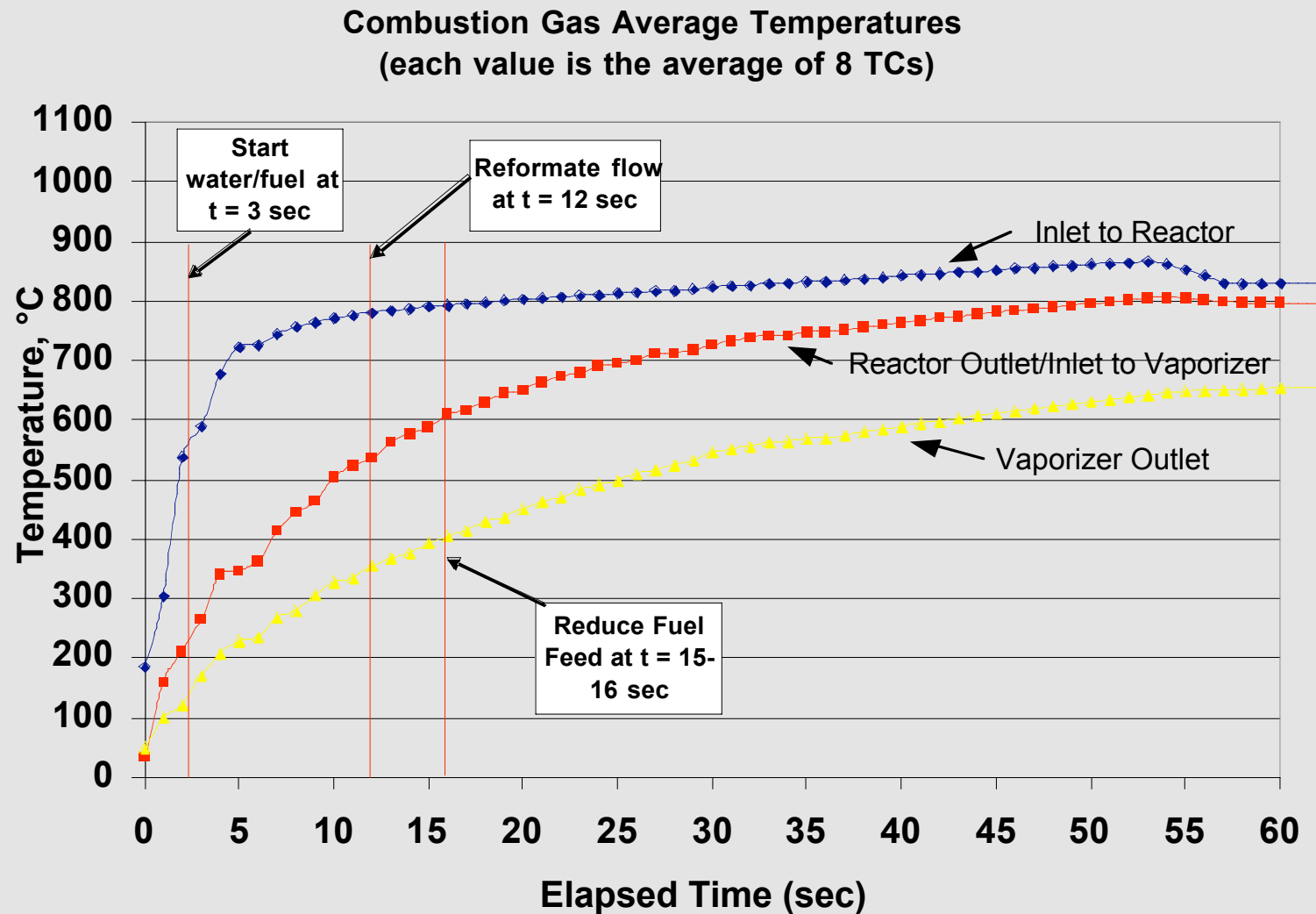


Recuperator Bypass valve

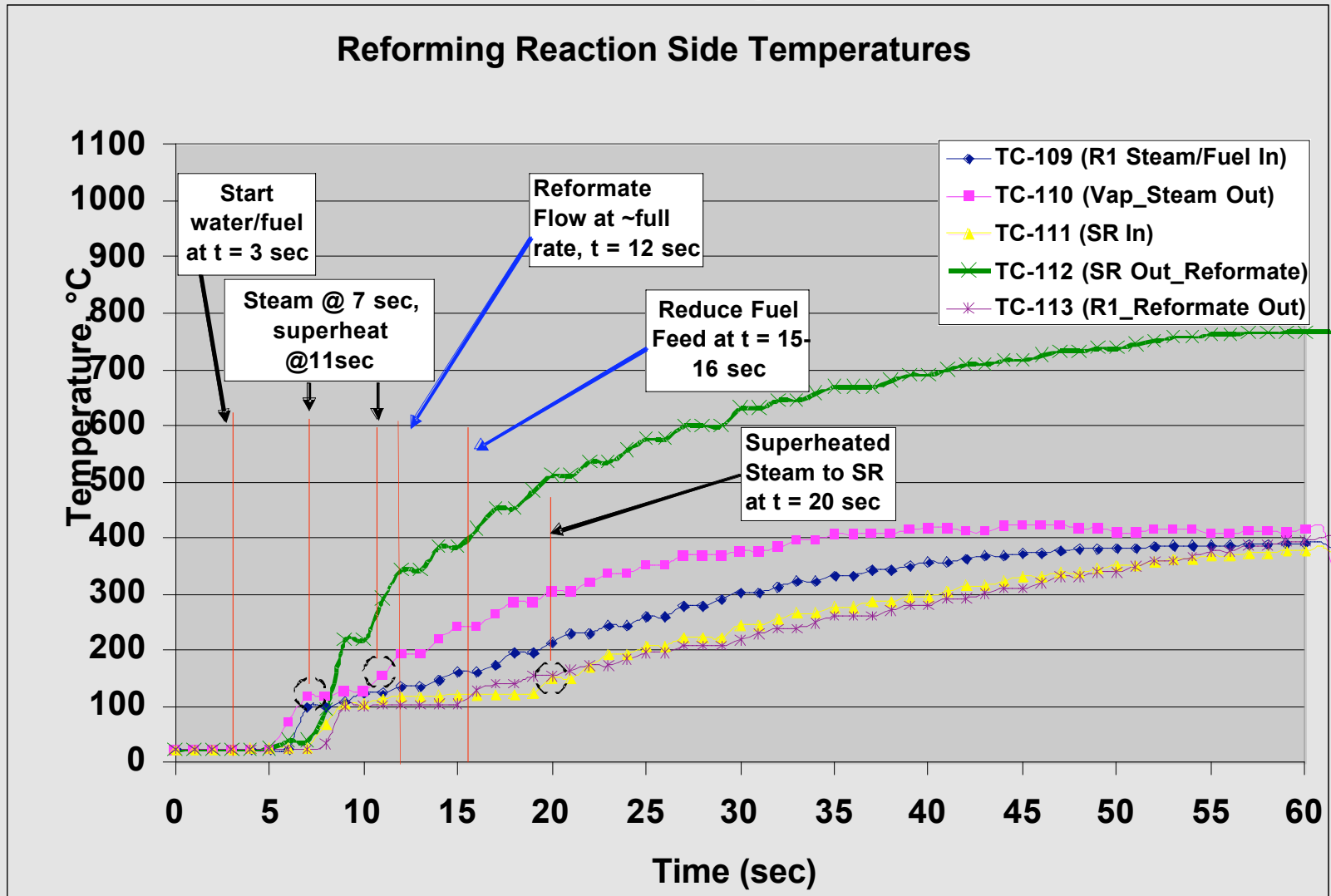
Fast Cold Start – Reformate Flow



Fast Start – Combustion Side Temperature

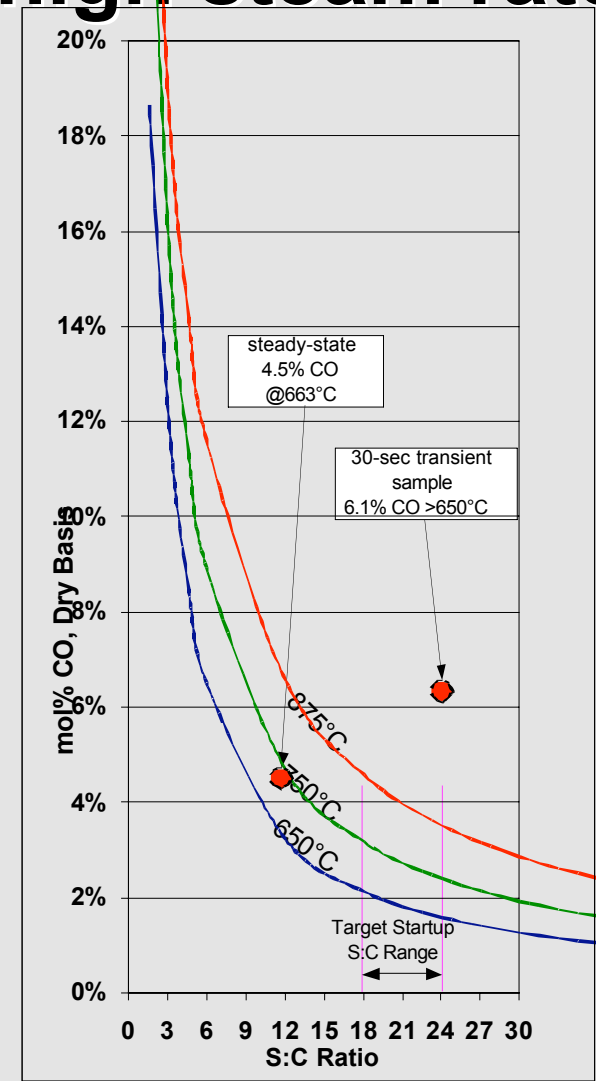


Fast Start - Reforming Side Temperatures



Start-up Strategy: Initially high steam rate

- ▶ At startup, heat from the reformer exhaust is used to make greater than normal (6-8X) quantities of steam.
- ▶ High steam flows heat the reformate recuperator (and WGS / PROX reactor once integrated.)
- ▶ Steam heating minimizes pressure drop on exhaust gas stream (compared to using exhaust gas directly).
- ▶ High steam flows provide high S:C ratio at reformer, reducing CO content in the reformate. Low CO reduces demand for WGS activity during startup.



Equilibrium CO concentrations

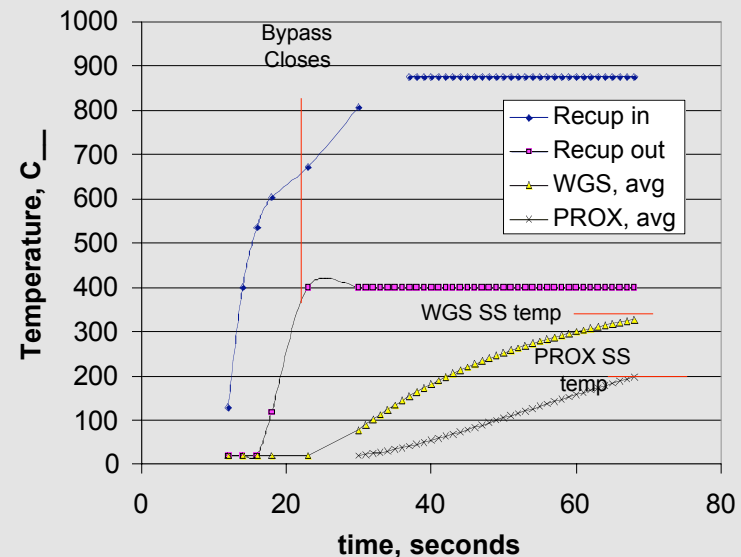
Pacific Northwest National Laboratory
U.S. Department of Energy

Preliminary Estimate of Warm up time for WGS/PROX

► Input Values/Assumptions

- Heat using heat capacity of high-steam (S:C=24:1) reformat. (neglect heat of reaction in WGS and PROX, heat on air side of WGS/PROX and condensation in initial operation).
- Extrapolate recuperator inlet temps to 875°C reforming temperature.
- Heat recuperator with bypass valve open, close when WGS inlet reaches 400°C, then control WGS inlet to 400°C.
- Simplified heat transfer model for each component.

With WGS/PROX reaction heat sources, system should reach operating temperature in < 60 s.



Development Path For Startup Approach

- ▶ Key improvement will be to reduce the air flow required during startup compared to initial prototype.
 - Transition to high temperature reforming. Reduces thermal mass of reformer by >3X.
 - Incorporate improvements in fabrication. Reduces mass of reformer panel by ~40%.
 - Utilize higher temperature combustion gas. Air flow reduced by up to a factor of 3 at 1500°C.
 - Continue to deliver sufficient heat to produce high startup steam rate. Limits extent of air flow reduction.
 - Reductions in air flow will reduce pressure drops and electrical power demand for blower.
- ▶ 50 kWe Startup Air Flow Target 450 – 600 scfm, with pressure drop of 5 to 10 inches water.

Thermal Mass Energy Estimates (thermal mass defines lower limit on startup energy)

50 kWe Projections for Thermal Mass Energy Requirement by Component

Device	Mass [kg]	Avg Operating Temp [°C]	Duty Required to heat from ambient [MJ]
Inconel 600 Steam Reformer (low-dP) (a)	5.5	875	2.09
Water Vaporizer (low dP) (b)	7.4	300	1.04
Air-Air Preheater (low dP) (b)	24.7	100	0.97
Reformate Recuperator (c)	1.8	554	0.48
WGS (differential) (d)	9.0	343	1.50
PROX (c)	6.6	200	0.90
Total			6.97

(a) projected based on current low dP design, temperature dependence demonstrated in earlier reactor design and demonstrated ability to reduce reduced bonding edge metal.

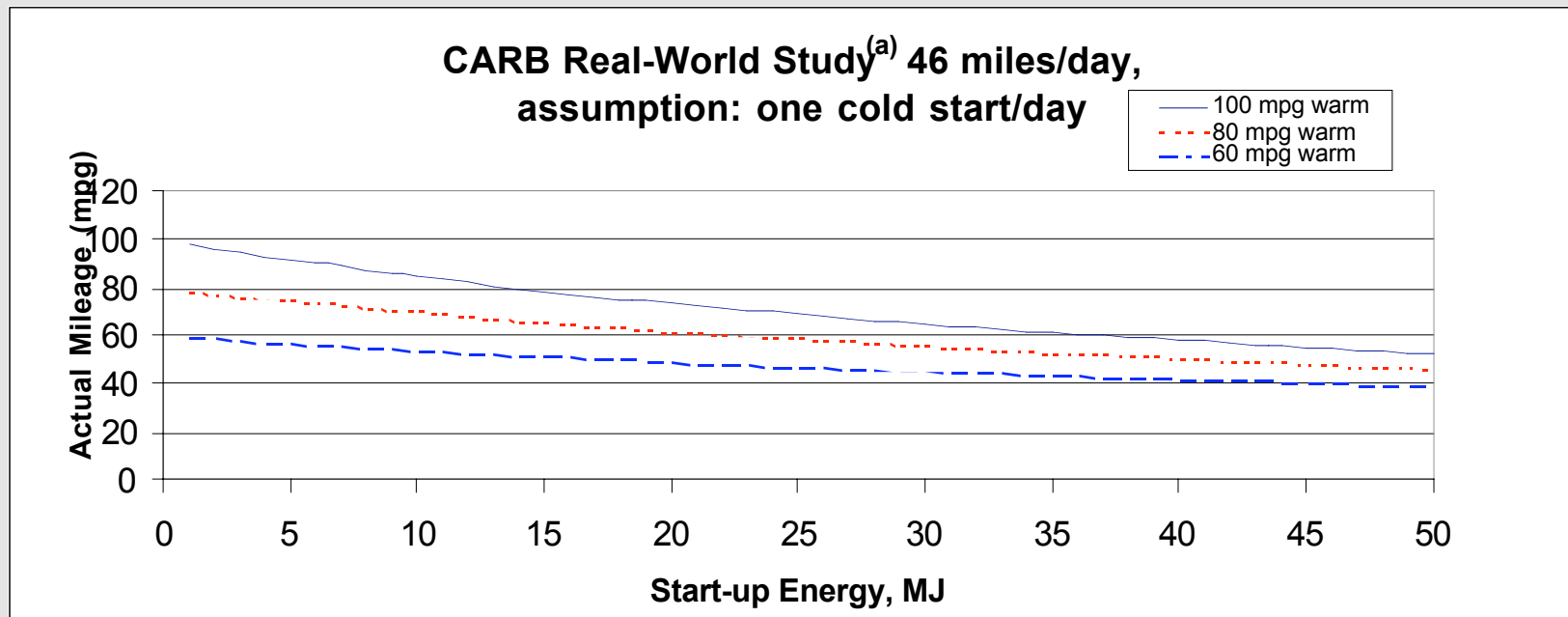
(b) linear extrapolation of 2 kWe prototype weight by power level. Actual weight may be less when scaled up to 50 kWe.

(c) estimated based on preliminary design

(d) based on linear scaling of core design for 2 kWe prototype to 50 kWe plus header and edge metal contributions

Mileage Penalty Due to Start-up Energy

- ▶ Target of 2 MJ, minimizes effect on fuel mileage.
- ▶ Insulating high temperature components so that only the first start each day is “cold” reduces impact.

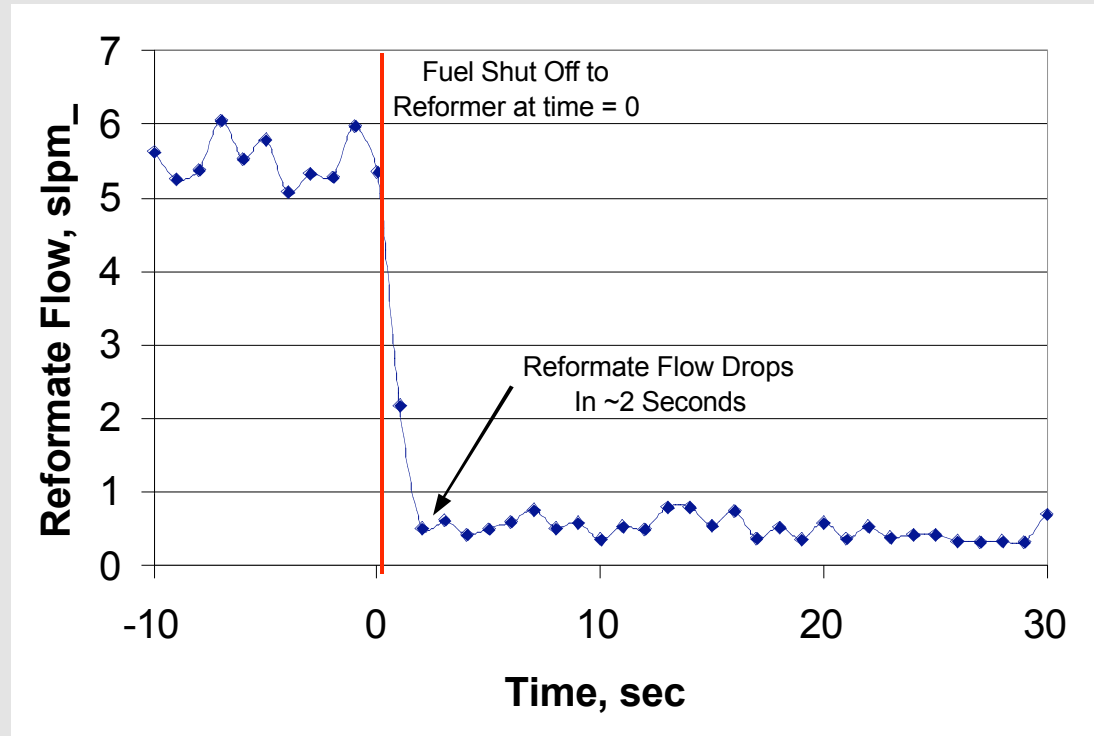


(a) Reference: Magbuhat, S., J. R. Long, California Air Resources Board, El Monte CA 91731: Improving California's Motor Vehicle Emissions Inventory Activity Estimates Through the Use of Data Logger-Equipped Vehicles. Presented at the 6th On-Road Vehicle Emissions Workshop, San Diego, CA, March 18-20, 1996.

Technical Accomplishments/Progress

Warm Transient Response

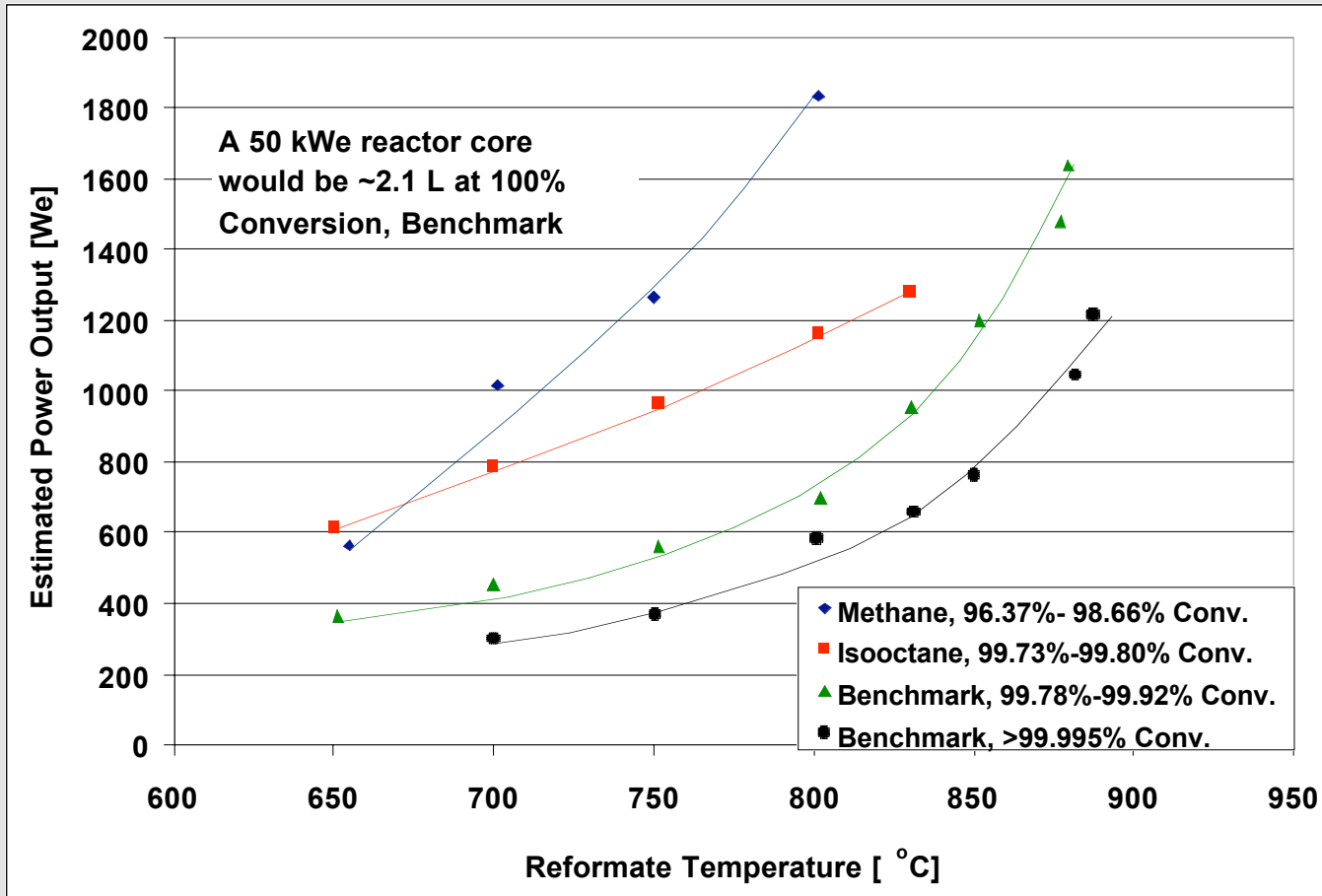
- ▶ Very short residence time within reformer enables rapid transient response.
- ▶ Direct liquid fuel injection reduces transient response compared to separate fuel vaporizer. (~2 second downward transient demonstrated).



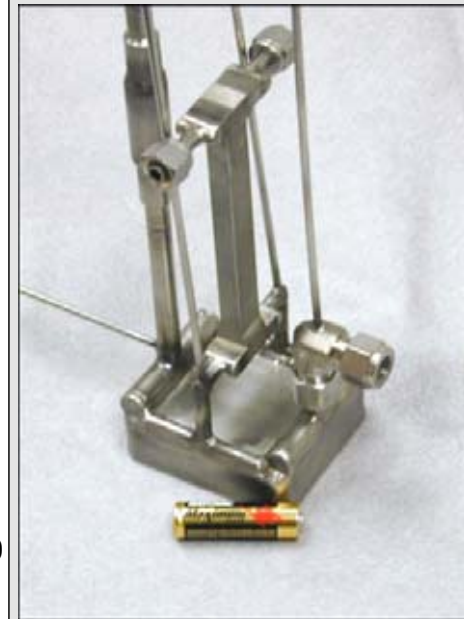
Transient with Direct Fuel Injection Into Steam

Previously Demonstrated Reformer Productivity vs Temperature

(All fuels at 3:1 S:C, CH₄ conv. is % approach to equil., Inconel 625 reformer)



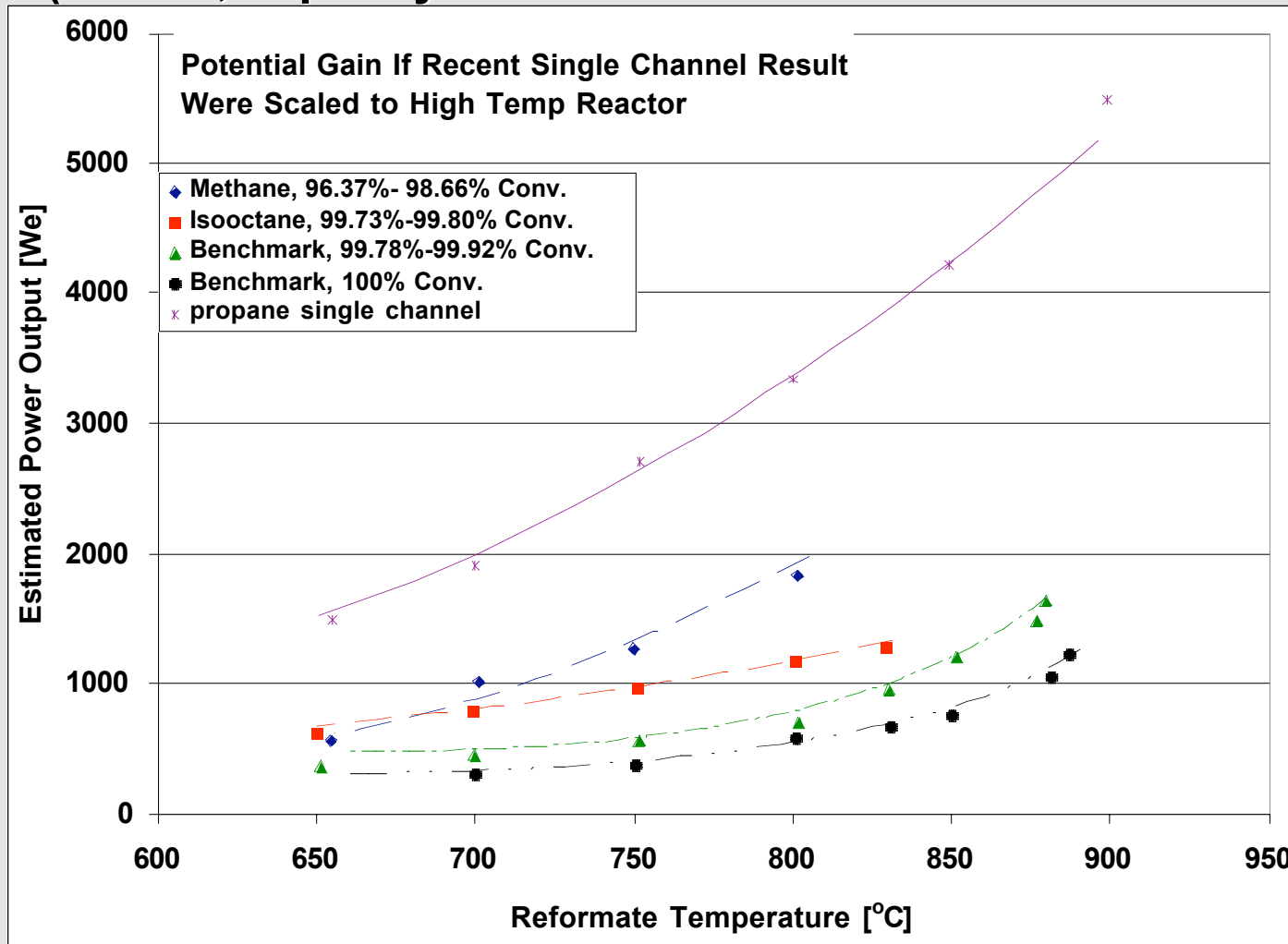
Inconel 625
High-
Temperature
Reformer



Stability of catalyst productivity verified by measuring the conversion at a reference condition before and after generation of the data for each curve.

Extrapolation of Recent Single Channel Propane Reforming Test Results

(3:1S:C, capacity evaluated at 99.7 to 99.8% conversion)



Removal of H₂S from Reformate

Testing performed on sulfur removal from simulated reformat stream using ZnO and CuY Zeolite.

Conclusions from testing include:

- ▶ The presence of H₂O and CO in the reformat stream make it difficult to achieve sub-ppm H₂S levels at WGS inlet conditions using ZnO.
- ▶ There is no advantage in using a differential temperature approach when removing H₂S with ZnO ahead of WGS reactor.
- ▶ Preferred approach with ZnO is to substantially cool the reformat, remove sulfur at minimum temperature, then reheat.
- ▶ CuY Zeolite can reduce sulfur levels from 25ppm to <150 ppb at ambient temperature. Material is not suitable at WGS temperature.

Comparison to DOE Performance Targets

Attribute	Units	2004 Status	2004 Demo Criteria	Ultimate Target
Transient	sec	~2, 100% to 10% ~5, 10% to 90%	<5, 10% to 90% and 90% to 10%	<1, 10% to 90% and 90% to 10%
Start-up Time (+20°C)	sec	12 sec at reformer , estimate <60 sec for full fuel processor	<60 to 90% traction power	<2 to 10%, <30 to 90%
Start-up	MJ/50kWe	>7.0 (a)	<2	<2
Efficiency	%	78 (b)	78	>80
Power density	W/L	2307 (c)	700	2,000
Durability	hours	1000+	2000h and >50 stop/starts	5,000h and 20,000 starts
Sulfur Tolerance	ppb	(d)	<50 out from 30 ppm in	<10 out from 30 ppm in
Turndown	ratio	>10:1	20:1	>50:1

(a) value is based on thermal mass of individual components and represents a minimum value.

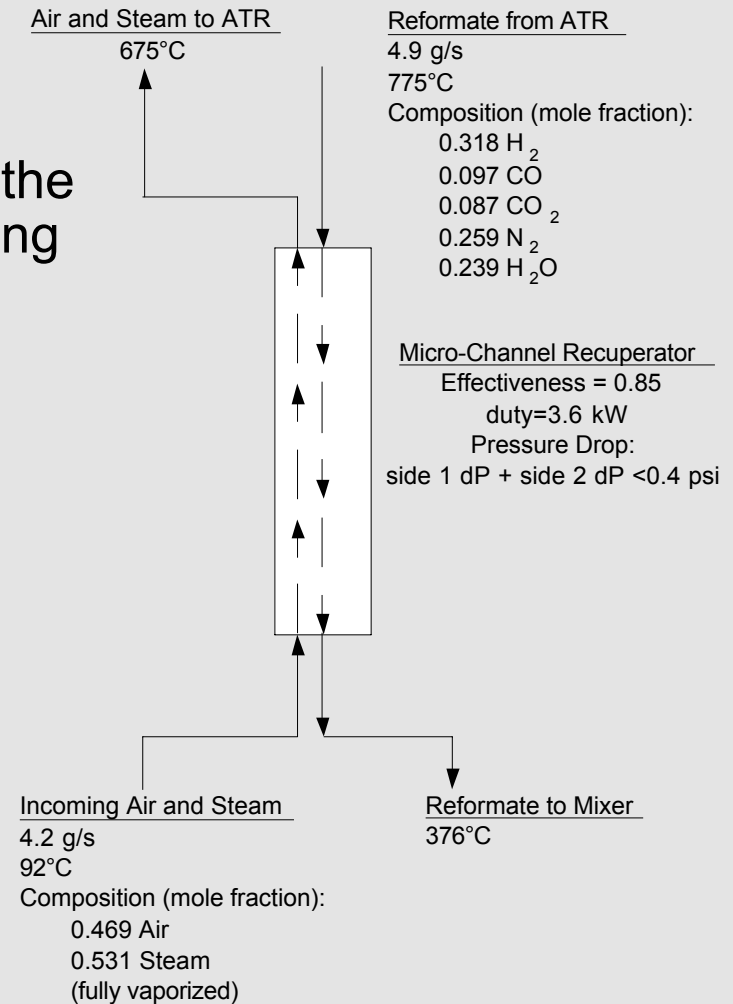
(b) calculated based on $0.95 \cdot (\text{LHV } \text{H}_2 \text{ out}) / (\text{LHV combustion fuel feed} + \text{LHV reforming fuel feed})$. The derating factor of 0.95 is considered very conservative for low dP system.

(c) based on individual components. Specific power estimated to be 909 We/kg on same basis. Does not include connecting duct and tubing instrumentation and insulation.

(d) Ability to provide <150 ppb reformate from 25 ppm reformate demonstrated at ambient. Issues remain with operation on 30 ppm fuel in reformer and removal ahead of WGS reactor.

Delivered Microchannel Recuperator for ANL FASTER ATR Reformer

- ▶ Preheats air and steam while cooling reformat to WGS temperature
- ▶ Includes a mixer to uniformly mix air into the reformat during startup to assist in heating WGS catalyst.



Interactions and Collaborations

- ▶ Delivered Recuperator/Mixer for 10 kWe FASTER autothermal reformer being developed at ANL.
- ▶ Providing micro-channel low-dP vaporizer to support testing of Catalytica 3 kWe steam reforming system.
- ▶ Working with the Gas Technology Institute and Cleaver Brooks to demonstrate HX technology in boiler economizer application.
- ▶ Micro-technology Intellectual property licensed to Velocys for specific fields of use, recent velocys activities
 - Velocys and ConocoPhillips, the largest U.S. refiner, have formed a joint venture to develop and commercialize a low-cost, modular hydrogen production process based on microtechnology.
 - The U.S. Department of Energy has selected the team of Velocys, Dow Chemical Company and Pacific Northwest National Laboratory to apply microchannel process technology to the production of ethylene and other olefins.
- ▶ PNNL has collaborated with Oregon State University to form the Micro-Products Breakthrough Institute

Reviewer Comments from FY2003

- ▶ *“Why stop at 2 kWe? The goal should be to design for 50 kWe system.”*

Response: Testing at smaller scale reduces cost associated with component development. Due to the nature of the microchannel approach, scaling is straight forward. A full scale water vaporizer was delivered to McDermott for inclusion in their demonstration.

- ▶ *“Weight reduction issues by applying material other than stainless steel should be addressed”*

Response: Currently pursuing high temperature Inconel reforming approach. This is expected to reduce reformer mass by ~4X. Also improvements in fabrication technique have eliminated unnecessary metal and reduced total reformer metal by ~40%. Additional work using light weight metals such as aluminum and titanium will be pursued as needed to support fuel processor development.

Future Work

- ▶ Assemble Inconel low-dP reforming reactor system
 - Demonstrate fast cold start and steady operation at 900°C
 - Demonstrate ability to utilize very high temp combustion gas
 - Demonstrate reduction in fast start fuel consumption
- ▶ Integrate with WGS reactor at 2 kWe scale
 - Demonstrate rapid start with reformer/WGS including ability to rapidly steam heat the WGS reactor
 - Evaluate the startup time, energy, and CO content vs time for this system.